LA-UR -80-500

CONF-800616--2

TITLE: INTERFACING PRIMARY HEAT SOURCES AND CYCLES FOR THERMOCHEMICAL HYDROGEN PRODUCTION

AUTHOR(S): Melvin G. Bowman

MASTER

SUBMITTED TO: 3rd World Hydrogen Energy Conference, Tokyo, Japan,
June 23-26, 1980

DISCLAIMER

[illegible]

By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes.

The Los Alamos Scientific Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

University of California

LOS ALAMOS SCIENTIFIC LABORATORY
Post Office Box 1663 Los Alamos, New Mexico 87545
An Affirmative Action/Equal Opportunity Employer

[illegible] IS UNLIMITED

INTERFACING PRIMARY HEAT SOURCES AND CYCLES FOR THERMOCHEMICAL HYDROGEN PRODUCTION

Melvin G. Bowman

University of California
Los Alamos Scientific Laboratory
Los Alamos, New Mexico, U.S.A. 87545

ABSTRACT

Advantages cited for hydrogen production from water by coupling thermochemical cycles with primary heat include the possibility of high efficiencies. These can be realized only if the cycle approximates the criteria required to match the characteristics of the heat source. Different types of cycles may be necessary for fission reactors, for fusion reactors or for solar furnaces.

Very high temperature processes based on decomposition of gaseous H_2O or CO_2 appear impractical even for projected solar technology.

Cycles based on CdO decomposition are potentially quite efficient and require isothermal heat at temperatures that may be available from solar furnaces of fusion reactors.

Sulfuric acid and solid sulfate cycles are potentially useful at temperatures available from each heat source. Solid sulfate cycles offer advantages for isothermal heat sources.

All cycles under development include concentration and drying steps. Novel methods for improving such operations would be beneficial.

KEYWORDS

Thermochemical hydrogen; synfuels from fusion; solar fuels; hydrogen energy; process heat applications.

INTRODUCTION

The possible advantages of thermochemical cycles for utilizing a primary heat source for the decomposition of water have been described several times in glowing terms. One advantage frequently cited is the fact that (in contrast to electrical power production) a "topping cycle" is not required for the efficient utilization of heat from high temperature heat sources. The statement is valid, but it must be emphasized that high efficiencies can be achieved only if the reaction temperatures and heat requirements of the cycle match the maximum temperature and heat delivery characteristics of the heat source. Therefore, it is of interest to consider the criteria for ideal cycles in terms of their potential for practical adaptation to available heat sources.

IDEAL CYCLE CRITERIA

One method for selecting cycles for specific maximum temperatures has been presented previously (Bowman, 1974) in terms of thermodynamic criteria for "ideal" cycles. It is presented again here as background for the consideration of problems of interfacing water splitting cycles with heat sources such as high temperature fission reactors, fusion reactors and solar concentrator systems.

Consider a two-step (single temperature cycle) process in which a reactant (R) reduces water at a low temperature (T_1) to evolve hydrogen and form the compound RO (R may also be an oxide), followed by thermal decomposition of RO at high temperature (T_2) with the evolution of oxygen. The reactions can be written as:

$$R + H_2O \rightarrow RO + H_2 \text{ at } T_1 \qquad (1)$$

$$RO \rightarrow R + 1/2\ O_2 \text{ at } T_2 \qquad (2)$$

If an ideal cycle is considered to be one in which $\Delta G^o = 0$ for all reactions, and if one utilizes the approximation

$$\Delta G^o T = \Delta H^o_{298} - T \times \Delta S^o_{298}$$

"ideal" values for entropies and heats of formation (from $R + 1/2\ O_2$) of the compound RO are approximately defined by the expressions:

$$\text{"ideal"} \Delta S^o F = \frac{\Delta G^o_F (H_2O) : \text{at } T_1}{(T_2 - T_1)}$$

$$\text{"ideal"} \Delta H^o_F = \Delta S^o \times T_2$$

where $\Delta G^o_F(H_2O)$ is the free energy of formation of water at T_1 (the low temperature). To illustrate, if we assume T_1 = 400 K (where $\Delta G^o_F(H_2O)$ = -224 kJ), and assume different temperatures for T_2, the corresponding parameters computed for RO are those given in Table 1.

TABLE 1

T_2	$-\Delta S^o{}_F(RO)$	$-\Delta H^o_F(RO)$
1200	280 J/K	336 kJ
1500	204	306
2000	140	280
2500	107	268

Since entropies of formation of oxides (per oxygen atom) are characteristically near -100 J/K, it is clear that very high temperatures will be required for two-step oxide cycles. This observation is the basis for published statements that two-step cycles are not feasible. Actually, two-step cycles are possible, in principle, even for relatively low maximum temperatures if one can identify usable reactions with the necessary large entropy changes. It should be recognized that the values in Table 1 are minimum absolute values. Low temperature reactions cannot realistically be expected to occur at a reasonable rate unless the free energy change is negative by a significant amount. Therefore, the low temperature reaction (or reactions) will be more exothermic than reaction 1 and the high temperature reaction or reactions will be more endothermic than indicated by reaction 2. It should be emphasized that the above treatment tacitly assumes that the reactions occur isothermally at the specified temperatures. When the cycle contains additional endothermic steps at lower than the maximum temperature, or if the reaction occurs over a temperature range (e.g., shifting equilibria for gas phase reactions), ΔS^o and ΔH^o requirements will be larger than values in Table 1 for the indicated maximum temperature. Consequently, the "ideal efficiency" or figure of merit will be lower.

HEAT SOURCE CHARACTERISTICS

Until relatively recently, high temperature gas cooled reactors were the "target" heat sources for thermochemical hydrogen cycles. The best known prototype reactor of this type is the AVR at Jülich. This reactor has an excellent operating record with an outlet helium gas temperature of ~1225 K and an inlet temperature of 550-600 K (Schulten, 1978). Thus in order to interface well, a thermochemical cycle for this heat source should contain an endothermic step or steps to accept heat relatively uniformly over the indicated temperature range. It is usually assumed that an intermediate heat exchanger will be required between the reactor gas stream and the chemical process loop with a resultant decrease in the upper useful temperature. However, "advanced" reactor fuels are essentially demonstrated and it is not too optimistic, perhaps, to assume process heat temperatures near 1300 K.

Recent and current studies have been concerned with synthetic fuels production from fusion reactors. It is usually recognized that hydrogen is the "prime" synthetic fuel and conceptual processes have been developed for coupling high temperature heat from fusion reactor blankets with thermochemical hydrogen cycles (Booth and colleagues, 1978) and with the high temperature electrolysis of steam (Fillo and colleagues, 1978). From these studies, it appears outlet temperatures of ~1600 K could be achieved with circulating inert gas or liquid metal systems. In a recent study, Pendergrass (1979) has analyzed the characteristics of process heat potentially available from fusion reactor blankets. From this study it seems reasonable to assume that nearly isothermal process heat can be extracted by systems based on metal liquid/gas vaporization/condensation systems at temperatures of, perhaps, ~1700 K or even higher.

The utilization of solar energy for the production of fuels and chemicals is a popular concept that appears to be attracting an increasing constituency. Certainly the concept merits serious consideration despite the fact that solar concentrator systems are expensive and solar heat intermittent. From the viewpoint of process heat for thermochemical hydrogen production, it is important to note that solar thermal systems can deliver near isothermal heat at very high temperatures. Therefore, high efficiencies (almost necessary for solar thermal processes) could be realized for cycles that approximate the ideal criteria described above and also interface well with a solar furnace. Temperatures available for practical processes are still uncertain. It is obvious that materials problems become increasingly difficult at very high temperatures. Further, at some point, radiation losses from central receiver targets will increase rapidly and overshadow any advantage of increasing temperature for a process. Certainly, maximum practical temperatures will be well below computed equilibrium or stagnation temperatures for solar furnaces.

CYCLE TYPE VERSUS TEMPERATURE DOMAIN

As indicated in the introduction, high efficiencies for thermochemical cycles can be achieved only if the temperature and heat delivery characteristics of the heat source approximate the requirements of the cycle. Therefore, it is instructive to consider the suitability of the heat sources to specific cycles requiring different maximum temperatures.

Direct Decomposition of H_2O and CO_2

The decomposition of $H_2O(g)$ has been proposed several times. It is clear that the low entropy change associated with this homogeneous decomposition reaction implies a low reaction yield even for the maximum credible temperature listed for a practical solar heat source. Fletcher and Moen (1977) have proposed operation at low pressures to enhance reaction yields. They have also recognized the necessity of separating the hydrogen and oxygen at temperature in order to avoid the extremely rapid back reaction as the gases are cooled and have proposed a separation based on the difference in effusion rates through a ceramic membrane or gauze. However, for temperature limitations imposed by materials properties as well as radiation losses, decomposition yields remain low (even for the proposed low pressures) and realistic assessments indicate efficiencies for heat utilization are too low for practicality.

The direct thermal decomposition of carbon dioxide seems to offer advantages over water decomposition for a high temperature process. Because of a larger decomposition entropy, at temperatures above 1100 K decomposition yields are significantly higher. The dry gases could be quenched to lower temperatures by means of a nozzle expansion without excessive back reaction. However, in order for this process to be of value, a practical low temperature method for separating carbon monoxide from oxygen and for separating carbon dioxide from hydrogen would be required. Further, it would be necessary to dry the carbon dioxide before each high temperature step since traces of water greatly accelerate the oxygen-carbon monoxide reaction at high temperature.

In summary, it seems probable that the problems associated with the direct decomposition cycles are, and will continue to be, more difficult than problems associated with including additional reactions in cycles that permit lower temperature operation and still yield high efficiencies if the ideal cycle criteria can be approximated.

Oxide Decomposition Cycles

As indicated above, solid oxide decomposition reactions exhibit entropies near 100 J/K (per oxygen atom). Thus, an examination of Table 1 indicates a decomposition temperature near 2700 K for an oxide suitable for a two-step cycle. However, some oxides exhibit larger entropies and consequently lower decomposition temperatures. A two-step iron oxide cycle has been proposed several times for use with solar heat. The cycle may be described by the following reactions:

$$3FeO + H_2O \rightarrow Fe_3O_4 + H_2 \qquad (3)$$

$$\Delta H^o_{(298)}\text{: with } H_2O(\ell) = -19 \text{ kJ}, \ \Delta S^o = +24 \text{ J/K}$$

$$\text{with } H_2O(g) = -63 \text{ kJ}, \ \Delta S^o = -95 \text{ J/K}$$

$$Fe_3O_4 \rightarrow 3FeO + 0.5\ O_2 \qquad (4)$$

$$\Delta H^o_{298} = +305\ kJ,\ \Delta S^o = +139\ J/K$$

Decomposes to $FeO_{(1+x)}$ liquid at ~2150 K

Reaction (3) is a known reaction. Reaction (4) (written as a solid decomposition reaction) exhibits one of the largest entropy changes known for this type of reaction. At first glance the cycle seems promising, but as one should expect, and as Tofighi (1978) and colleagues found, Fe_3O_4 melts before it decomposes and oxygen evolution is over a relatively narrow liquid homogeneity range. It is unfortunate, perhaps, that Fe_3O_4 melts before it decomposes since suitable substitutes for Fe_3O_4 in this type of cycle have not been identified.

A second type of two-step, oxide cycle includes a solid decomposition reaction to form two gaseous products rather than a condensed phase and gaseous oxygen. The extra gaseous product increases the decomposition entropy and this implies a lower temperature process. The concept can be illustrated by the following equations (where M is a metal),

$$M(s) + H_2O \rightarrow MO + H_2 \qquad (at\ T_1) \qquad (5)$$

$$MO \rightarrow M(g) + 1/2\ O_2 \qquad (at\ T_2) \qquad (6)$$

Typical ΔS^o 200 -210 J/K

If the typical ΔS^o for reactions presented by equation (6) is compared with values listed in Table 1, a temperature difference of 1100° is implied for this cycle. However the high temperature endothermic heat requirement includes the sum of the heat of sublimation of the metal plus $-\Delta H^o_f$ (MO) and higher values of T_2 will be required for the $T_2 \times \Delta S^o$ term to match the overall ΔH^o. Since entropies of vaporization for metals are fairly similar, the ideal metal for this type of cycle would be one with a low boiling point (to minimize heat of vaporization) that would just reduce water at low temperature. Cadmium and zinc are two candidates frequently mentioned for this type of cycle. Neither is an ideal candidate although both have relatively low boiling points. Published boiling points and oxide decomposition temperatures are as follows:

CdO: Td = ~1750 - 1850 K, BP (Cd) = 1038 K

ZnO: Td = ~2300 K, BP (Zn) = 1180 K

From published thermochemical data, reaction (5) with Cd should not be expected and, in fact, does not occur. However, Pangborn (1976) described an electrochemical method for promoting the reaction. The proposed cycle was not developed into an actual process since projected gas cooled reactors (the "target" heat sources at that time) were not suitable for the high temperature isothermal step, even for the lower CdO decomposition temperatures sometimes reported.

In contrast to the Cd cycle, reaction (5) with Zn is very exothermic. This difference is reflected in the much higher oxide decomposition temperatures. Since back reaction between oxygen and gaseous metal atoms must be minimal, the high decomposition temperature for ZnO implies a very difficult cycle even if the high temperature isothermal heat source is available. Therefore, despite the difficult low temperature reaction, cadmium appears to be the best candidate for this type of cycle. At LASL, a "pure" thermochemical cycle is under study that also incorporates the decomposition of cadmium oxide (Mason, 1980). It may be described by the following reactions:

$$Cd + H_2O + CO_2 \rightarrow CdCO_3 + H_2 \quad \text{(low temp.)} \tag{7}$$

$$CdCO_3 \rightarrow CdO + CO_2 \quad (\sim 575\ K) \tag{8}$$

$$CdO \rightarrow Cd(g) + 1/2\ O_2 \quad (1600\text{-}1800\ K) \tag{9}$$

$$Cd(g) \xrightarrow{1400} Cd(\ell) \xrightarrow{595\ K} Cd(c) \tag{10}$$

Reaction (7) to form the carbonate does take place, but the yield is limited by the formation of a protective layer of carbonate on the cadmium metal. However, encouraging results have been achieved in reactions where NH_4Cl is used as a catalyst for the reaction. The cadmium oxide based cycles offer the potential for high efficiency if:

(1) Solar heat or fusion heat can be utilized effectively for the oxide decomposition step.
(2) The back reaction between cadmium vapor and oxygen is sufficiently slow.
(3) The low temperature reaction can be conducted at a practical rate and the resultant solid does not adsorb or occlude too much water.

Sulfuric Acid - Metal Sulfate Cycles

These cycles were developed from attempts at LASL to use the criteria described above to identify cycles with a minimum number of reaction steps and maximum temperatures below 1300 K. Since ΔS^o values for decomposition reactions increase with the number of gaseous molecules evolved, our early studies were directed toward cycles involving the decomposition of sulfates(Bowman, 1974). The concept can be illustrated by the following equations:

$$MO + SO_2 \rightarrow MSO_3 \quad \text{(low temp.)} \tag{11}$$

$$MSO_3 + H_2O \rightarrow MSO_4 + H_2 \quad \text{(low temp.)} \tag{12}$$

$$MSO_4 \rightarrow MO + SO_2 + 0.5\ O_2 \quad \text{(high temp.)} \tag{13}$$

$$\text{Typical } \Delta S^o \quad 275\text{-}290\ J/K$$

From the typical ΔS^o of the overall sulfate decomposition, an inspection of Table 1 indicates the possibility of a two-step cycle with an "ideal" temperature difference of 800° between low temperature and high temperature reactions. Of course, larger temperature differences would be necessary.

It should be noted that reactions (11) and (12) do not represent equilibrium chemistry. For equilibrium at low temperature the sulfite should undergo one of the following reactions.

$$MO + SO_2 \rightarrow 0.75\ MSO_4 + 0.25\ MS \tag{14}$$

$$MO + 1.5\ SO_2 \rightarrow MSO_4 + 0.5\ S \quad . \tag{15}$$

Further, if hydrogen were evolved in reaction (12) it could reduce the metal sulfite according to the equation:

$$MSO_3 + 3H_2 \rightarrow MS + 3H_2O \quad . \tag{16}$$

However, most sulfites form and decompose without evidence of the equilibrium reactions. Thus, we were encouraged to attempt to promote reaction (12) in many different sulfate systems representing a wide range of stability. Our results have never included significant hydrogen yields. In most cases, the equilibrium reactions were also not observed.

As a variation of sulfate cycles we also studied cycles based on the formation and decomposition of sulfuric acid. Several reactions to form sulfuric acid solutions were promoted successfully. Such cycles are currently receiving the major fraction of the worldwide development effort commited to thermochemical hydrogen processes. It should be noted that the overall decomposition of sulfuric acid includes a solution concentration step, an evaporation step to form $H_2SO_4(g)$, a decomposition step to form $H_2O(g)$ plus $SO_3(g)$ and the decomposition of SO_3 to form SO_2 plus 0.5 O_2. Since homogeneous decomposition reactions occur over significant ranges of temperature, the overall process accepts heat over a wide temperature range with the maximum temperature dependent on the pressure of the system. Thus, sulfuric acid cycles are compatible with the heat delivery characteristics of gas-cooled reactors. However, it should also be noted that processes to form sulfuric acid yield the acid in solution and significant energy is required to concentrate the acid prior to the decomposition step. One potential method for reducing these energy requirements involves reacting the sulfuric acid solution with a metal oxide to form an insoluble metal sulfate, in principle the sulfuric acid concentration step can be eliminated and corrosion problems can be minimized since the sulfuric acid vaporization step is avoided and the final decomposition involves only the solid and dry gases. The application of the concept to the hybrid sulfuric acid cycle is described by the following equations:

$$SO_2 + 2H_2O \rightarrow H_2SO_4(sol) + H_2 \text{ (electro.)} \qquad (17)$$

$$MO + H_2SO_4 \rightarrow MSO_4 + H_2O \quad \text{(low temp.)} \qquad (18)$$

$$MSO_4 \rightarrow MO + SO_3 \quad \text{(high temp.)} \qquad (19)$$

$$SO_3 \rightarrow SO_2 + 0.5O_2 \quad \text{(high temp.).} \qquad (20)$$

For highest efficiencies, the metal sulfate should be insoluble, should not form a hydrate and should not require excessive heat for its decomposition (i.e., should decompose near the SO_3 decomposition temperature).

One potential solid sulfate system being studied at LASL (Cox and colleagues, 1980) involves the formation and decomposition of bismuth oxysulfate. The overall cycle includes the reactions

$$SO_2 + 2H_2O \rightarrow H_2SO_4 \text{ (sol.)} + H_2 \quad \text{(electro.)} \qquad (21)$$

$$H_2SO_4 \text{ (sol.)} + Bi_2O_2SO_4 \rightarrow Bi_2O(SO_4)_2 + H_2O \qquad (22)$$

$$Bi_2O(SO_4)_2 \rightarrow Bi_2O_2SO_4 + SO_2 + 0.5\ O_2 \sim 1050\ K. \qquad (23)$$

Since reaction (22) requires only relatively dilute sulfuric acid, it is possible that less electrical energy will be required for the electrolysis step (reaction (21) than is required for the hybrid sulfuric acid process.

It is interesting to note that the use of the solid sulfate alters the character of the heat desired for the cycle. To illustrate: If 1.14 moles of $Bi_2O(SO_4)_2$ were heated to 1125 K, the equilibrium dissociation pressure would be about 4.2 atmospheres and consist of 50% SO_2, 25% SO_3 and 25% O_2. If the evolved gases were then heated at constant pressure to 1300 K, the equilibrium would shift to 61% SO_2, 8.5% SO_3 and 30.5% O_2. The SO_3 would be 88% dissociated and a total of one mole of SO_2 produced. The total heat requirement would be about 270 kJ of near isothermal heat at 1125 K and an additional (net)23.6 kJ for the additional gaseous decomposition between 1125 and 1300 K. If one assumes that the total heat requirement is supplied by helium cooled from 1300 K to 1125 K, it would be necessary to circulate a minimum of 81 moles of He for each mole of SO_2 produced. In contrast, if 1.17 moles of $H_2SO_4(\ell)$ were heated to 700 K, the equilibrium pressure would be 10.6 atmospheres and consist of $H_2SO_4(g)$, H_2)(g), $SO_3(g)$ and small quantities of SO_2 and O_2. If the gases were then heated at constant pressure to 1300 K, the equilibrium composition would be approximately 41.2% $H_2O(g)$, 6% SO_3, 35.2% SO_2 and 17.6 O_2 and contain one mole of SO_2. The heat requirement would be about 114 kJ of near isothermal heat for the vaporization/decomposition step at 700 K and an additional net of 162 kJ for the additional gaseous decomposition between 700 and 1300 K. If one assumes that heat is supplied by helium cooled from 1300 to 700 K, it would be necessary to circulate a minimum of 19 moles of He for each mole of SO_2 produced. About 41% of the heat content of the circulating helium would be required for the isothermal step at 700 K. Thus, sulfuric acid decomposition does not couple ideally with heat delivered from a gas cooled reactor. However, it is a better match than the solid decomposition which will couple better with an isothermal heat source.

It should be emphasized, that relatively large quantities of energy are required for drying sulfuric acid solutions before the acid is vaporized and decomposed. In addition large quantities of energy are required for the overall process of forming sulfuric acid and evolving hydrogen whether it is via an electrochemical step or whether it includes a sub-cycle to form and decompose a hydrogen halide. The potential advantages of inserting the solid sulfate are primarily the possibility of reducing energy requirements for both operations.

Alternate Sulfate Cycles

Although bismuth sulfate was chosen as an example for the above discussion of sulfuric acid-solid sulfate cycles, it is possible that alternate sulfates may prove to be better for practical cycles.

Some of the sulfate decomposition reactions that have been considered for hybrid sulfuric acid-solid sulfate cycles are listed in Table 2. The overall heat

TABLE 2 Sulfate Decomposition to Form $SO_2 + 1/2\ O_2$

	Solid Phases	H^o_{298}(kJ)
1.	$BaSO_4 \rightarrow BaO$	585
2.	$CaSO_4 \rightarrow CaO$	510
3.	$1/3\ La_2(SO_4)_3 \rightarrow 1/3\ La_2O_3$	420
4.	$MgSO_4 \rightarrow MgO$	380
5.	$ZnSO_4 \rightarrow ZnO$	334
6.	$CuSO_4 \rightarrow CuO$	318
7.	$1/2\ La_2\ (SO_4)_3 \rightarrow 1/2\ La_2O_2SO_4$	(320 - 340)
8.	$Bi_2O(SO_4)_2 \rightarrow Bi_2O_2SO_4$	270
9.	$CaSO_4 + MoO_3 \rightarrow CaMoO_4$	336
10.	$1/3\ La_2(SO_4)_3 + MoO_3 \rightarrow 1/3\ La_2(MoO_4)_3$	(290)

requirement (ΔH^o_{298}) for each indicated decomposition reaction is also listed. It should be noted that ΔS^0 values for the decomposition reactions are quite similar. Hence a higher ΔH^o_{298} value implies a higher decomposition temperature and a lower overall efficiency. Consequently, from the viewpoint of efficieicy alone, the listed bismuth oxysulfate decomposition would be the reaction of choice. However, in addition to the fact that bismuth is quite expensive, there is the possibility that a more stable sulfate will be better suited to reducing the energy required for some overall process to form dilute sulfuric acid and evolve hydrogen. The elimination of sulfuric acid as an intermediate might be sufficiently advantageous to justify use of the more stable sulfates that would require isothermal heat from solar furnaces or an advanced "heat pipe" system for extracting heat from the blanket of a fusion reactor or from a very high temperature fission reactor. Continuing studies are being made to evaluate the advantages of alternate sulfates (Hollabaugh, 1980).

Low Temperature Cycles

From the previous discussion, and the projected availability of high temperature heat sources, one might conclude that there is little motivation to develop thermochemical hydrogen processes for temperatures below 1200 K. However, it is also true that lower temperatures can simplify materials and process problems. Therefore, since optimized high temperature cycles have not been demonstrated, low temperature cycles (below 1000 K) may still merit attention.

During the 2nd World Hydrogen Energy Conference, Kondo and colleagues (1978) described a low temperature magnesium-iodine cycle. Appleman and colleagues (1978) presented a low temperature mercury-iodine cycle. Both cycles include extensive evaporation from solution. From the viewpoint of engineering efficiency and costs, solution evaporation steps are disadvantageous. Nevertheless, it must be recognized that every cycle under practical development at this time includes such steps. Therefore, it would be prudent for the thermochemical hydrogen community to identify and develop general methods for improving process features of solution chemistry. For example, it would be useful to seek solution processes that permit phase separation rather than solvent evaporation. It is certainly obvious that better methods for processing solutions would improve present thermochemical cycles and also extend the range of temperatures for interfacing thermochemical cycles with different heat sources.

REFERENCES

Bowman, M.G. (1974). Fundamental aspects of systems for the thermochemical production of hydrogen from water. *Proceedings of the First National Topical Meeting on Nuclear Process Heat Applications*, Los Alamos, New Mexico. (Los Alamos Scientific Laboratory Report, LA-5795-C).

Schulten, R. (1978). Nuclear energy as a primary energy source for hydrogen production. *Proceedings of the 2nd World Hydrogen Energy Conference*, Zurich, Switzerland.

Booth, L. A., M. G. Bowman, G. E. Cort, K. E. Cox, D. J. Dudziak, R. A. Krakowski, J. H. Pendergrass and A. S. Tai (1978). Production of electrothermochemical hydrogen using a fusion source of high-temperature process heat. *Proceedings of the 3rd American Nuclear Society Meeting on the Technology of Controlled Nuclear Fusion*, Santa Fe, New Mexico.

Fillo, J. A., J. R. Powell, M. Steinberg, F. Salzano, R. Benenati, V. Dang, S. Fogelson, H. Isaacs, H. Kouts, M. Kushner, O. Lazareth, S. Majeski, H. Makowitz, T. V. Sheehan (1978). Hydrogen production from fusion reactors coupled with high temperature electrolysis. Proceedings of the 2nd World Hydrogen Energy Conference, Zurich, Switzerland.

Pendergrass, J. H. (1979). Fusion energy sources for driving thermochemical cycles. Los Alamos Scientific Laboratory Report, LA-UR-79-3026.

Tofighi, A., O. Sibieude, M Duccarroir, and G. Benezerh (1978). Decomposition thermique a l'air de la magnetite au foyer d'un four solaire. Rev. Int. Htes Temp. et Refract, 15, 7-13.

Fletcher, E.A. and R. L. Moen (1977). Hydrogen and oxygen from water. Science 197, 1050.

Pangborn, J. B. (1976). Laboratory investigations on thermochemical hydrogen production. Proceedings of the 1st World Hydrogen Energy Conference, Miami, Florida.

Mason, C.F.V. and M. G. Bowman (1980). The cadmium-cadmium carbonate cycle for the thermochemical production of hydrogen. This Conference.

Cox, K. E., W. M. Jones and C. L. Peterson (1980). The LASL bismuth sulfate thermochemical hydrogen cycle. This Conference.

Hollabaugh, C. M., T. C. Wallace, Sr., M. G. Bowman and W. M. Jones (1980). The high temperature reactions of sulfates with molybdemun oxide. This Conference.

Kondo, W., S. Mizuta, T. Kumagai, Y. Oosawa, Y. Takemori and K. Fugii (1978). The magnesium-iodine cycle for the thermochemical decomposition of water. Proceedings of the 2nd World Hydrogen Energy Conference. Zurich, Switzerland.

Appleman, E. H., F. Schreiner and B. M. Abraham (1978). Experimental verification of the mercury-iodine thermochemical for the production of hydrogen from water, ANL-4. Proceedings of the 2nd World Hydrogen Energy Conference, Zurich, Switzerland.